Treatment of Liquid Waste of Remazol Blue Using Ozone Plasma Nanobubble Reactor

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Abstract. Textile wastewater contains hazardous chemicals that are toxic, carcinogenic, and difficult to degrade. To address these issues, a waste treatment method using Advanced Oxidation Processes (AOPs) technology, such as the Ozone Plasma Nanobubble Reactor (OPNR), was tested. OPNR is a new technology that has proven efficient in treating industrial wastewater, particularly dye liquid waste. The study tested the performance of OPNR in degrading Remazol blue wastewater, using non-thermal plasma to produce hydroxyl radicals, ozone, hydrogen peroxide, and other active species. The conditions for the study included a 1000 mL volume of liquid waste, with variations in gas fluid feed for ozone formation, gas flow rate, and plasma voltage. The results showed that at minimum conditions with a 60-minute degradation time, the percentage of Remazol blue degradation was 32.84%, while at optimum conditions with a 60-minute degradation time, the percentage was 100%.

Keywords: Ozone plasma nanobubble, Dielectric Barrier Discharge, Remazol blue, Textile wastewater, Degrade, Hydroxyl radical.

1. Introduction

Textile industry liquid waste, including Remazol Brilliant Blue R (RBBR), which mostly consists of dye residues, has the potential to pollute water and inhibit photosynthesis. Common textile waste treatment methods such as biological oxidation, physico-chemical treatment and adsorption are less effective due to the complex structures of dyes and high operating costs (He et al., 2008; Li et al., 2007). Modern approaches such as biodegradation, chlorination, and ozonation have been tested; however, they require higher operational costs, rendering them less effective (Setyaningtyas et al., 2012).

To address the limitations, the nanobubble plasma ozone technique can be utilised for the treatment of RBBR liquid waste. Ozone represents a potent oxidizer that is eco-friendly and does not generate any hazardous by-products. This study employs the Dielectric Barrier Discharge (DBD) plasma reactor, which can effectively cater to the needs of wastewater treatment processes owing to its application at atmospheric pressure levels and its

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widespread adoption across various industries. The voltage necessary for the plasma reactor significantly impacts the process, as the voltage level affects the plasma formation.

The OPNR is a newest innovation in the field of plasma, specifically for water and wastewater treatment technology. It autonomously generates ozone within the DBD reactor, eliminating the need for additional ozone generator instruments (Luvita et al., 2022). This makes it a recent advancement in ozone technology for waste processing. The utilization of nanobubbles can considerably enhance the effectiveness of wastewater treatment, lengthen reactor lifespan, and produce multiple free radicals, thereby achieving better overall reactor performance than previous models. Furthermore, introducing plasma into the mixture of nanobubbles on the surface of the water can enhance the efficiency of waste processing (Christianti, 2022).

2. Materials and Methods

2.1. Materials and Chemicals

Remazol Brilliant Blue R, air, sulfuric acid, potassium permanganate, sodium oxalate, aquades, ozone test kit, Nitraver® reagent and COD reagent were obtained from Process Intensification Technology Laboratory, Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia.

2.2. Ozone Plasma Nanobubble Reactor

The OPNR comprises of two components - a plasma DBD reactor made of quartz glass and a nanobubble nozzle. OPNR possesses a diameter of 5 cm and a height of 40 cm, and within it, a quartz glass barrier of 2 cm diameter works as a barrier. The positive electrode is fashioned from 30 turns of SS 316 stainless steel wire, while the negative electrode follows the shape of the tube, made from stainless steel mesh, and is located inside the glass tube. The nanobubble nozzle is a two-part system that uses the swirling flow method to introduce threads to the reactor, increasing turbulence in gas fluid flow. The liquid flows axially before being directed into the outer chamber by a conus (Luvita, 2022). The tangential flow from the directional hole creates a vortex flow in the inner chamber, causing a significant pressure gradient. The pressure reaches its nadir at the nozzle axis, while the tangential speed and turbulence level reach their zenith. The small input pressure of the gas fluid results in low energy consumption, making it a beneficial feature for the nozzle (Levitsky et al., 2016). The nozzle's design ensures efficient and efficient use of gas.

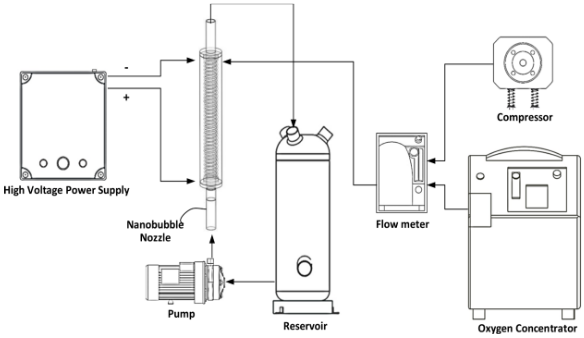

Fig 1. OPNR Configuration. (Luvita et al., 2022)

2.3. Analytical Methods

The initial tests carried out before degrading RBBR waste are reactor leak tests, hydroxyl radical quantification tests, and ozone solubility tests. After that, the RBBR waste degradation process was carried out with OPNR. Finally, a final test is carried out on the degradation results, namely pH test, nitrate content test, COD content test, and colour content test.

Reactor Leak Test

The reactor leak test assesses the condition of the OPNR and hose by using liquid fluid (water) and gas fluid (oxygen or air) to ensure that there are no leaks during the research.

Hydroxyl Radical Quantification Test

Hydroxyl radical quantification test aims to determine the number of hydroxyl radicals present in a sample. The hydroxyl radical is a highly potent oxidizing agent that is remarkably reactive and short-lived. When hydroxyl radicals combine, they create H_2O_2 compounds, which exhibit stability and durability. Furthermore, if the H_2O_2 concentration increases, so will the OH radical concentration. This examination employs the permanganometry technique, in which potassium permanganate, a strong oxidizing agent, acts as a titrant to titrate H_2O_2.

Ozone Solubility Test

OPNR generates ozone, which breaks down into hydroxyl radicals and acts as an oxidant in the degradation of RBBR waste. Ozone solubility is a crucial parameter for detecting its presence in liquid fluids. An ozone test kit, which includes N,N-diethyl-phenylenediamine (DPD), was employed to evaluate ozone solubility. The reaction between DPD and potassium iodide produces a purple colour, which intensifies with an increasing concentration of dissolved ozone. The UV-Vis Spectrophotometry method was used to measure the solution's absorbance at a wavelength of 550 nm.

RBBR Degradation

The waste to be degraded is RBBR with an initial concentration of 100 pm with a volume of 1000 ml. RBBR degradation was carried out with 18 different operating conditions, namely (1) using free air fluid with a flow rate of 2 liters/minute and a plasma voltage of 5 kV, (2) using free air fluid with a flow rate of 3 liters/minute and a plasma voltage of 5 kV, (3) using free air fluid with a flow rate of 4 liters/minute and a plasma voltage of 5 kV, (4) using free air fluid with a flow rate of 2 liters/minute and a plasma voltage of 10 kV, (5) using free air fluid with a flow rate of flow of 3 liters/minute and plasma voltage of 10 kV, (6) using free air fluid with a flow rate of 4 liters/minute and plasma voltage of 10 kV, (7) using free air fluid with a flow rate of 2 liters/minute and plasma voltage of 12 kV, (8) using free air fluid with a flow rate of 3 liters/minute and a plasma voltage of 12 kV, (9) using free air fluid with a flow rate of 4 liters/minute and a plasma voltage of 12 kV, (10) using oxygen fluid with a flow rate of 2 liters/minute and a plasma voltage of 5 kV, (11) using oxygen fluid with a flow rate of 3 liters/minute and a plasma voltage of 5 kV, (12) using oxygen fluid with a flow rate of 4 liters/minute and a plasma voltage of 5 kV, (13)) using oxygen fluid with a flow rate of 2 liters/minute and a plasma voltage of 10 kV, (14) using oxygen fluid with a flow rate of 3 liters/minute and a plasma voltage of 10 kV, (15) using oxygen fluid with a flow rate of 4 liters/minute and plasma voltage of 10 kV, (16) using oxygen fluid with a flow rate of 2 liters/minute and plasma voltage of 12 kV, (17) using oxygen fluid with a flow rate of 3 liters/minute and plasma voltage of 12 kV, and (18) using oxygen fluid with a flow rate of 4 liters/minute and a plasma voltage of 12 kV. Data was taken at 0, 15, 30, 45, and 60 minutes due to ozone has a residence time of approximately 15 minutes.

pH Test

The pH test was carried out at 0, 15, 30, 45, and 60 minutes under optimum operating conditions using a pH meter.

Nitrate Content Test

The RBBR waste degradation process produces acidic nitrate compounds, which can be analysed using the Nitraver® Nitrate Reagent Powder Pillows reagent. Nitrate levels are measured using a UV-Vis spectrophotometer at different time intervals, including 0, 15, 30, 45, and 60 minutes, under optimal operating conditions.

COD Content Test

Textile waste from the textile industry is a non-biodegradable compound. Chemical Oxygen Demand (COD) represents the oxygen volume demanded to oxidize organic substances present in water. The COD value is a crucial parameter to gauge the degree of pollution of liquid waste by organic substances, and as organic substances accumulate in waste, it poses a more significant threat to the environment. A solution's high COD value is indicative of its significant organic compound content. Using the UV-Vis spectrophotometry method, COD measurements for RBBR waste were performed at 0, 15, 30, 45, and 60-minute intervals under optimal operating conditions.

Platinum-Cobalt (Pt-Co) Scale Test

The Pt-Co scale is a tool used to assess pollution levels in liquid waste. It measures the intensity of yellow color samples by dilution of a 500-ppm platinum-cobalt solution. The colour produced by 1 mg of Pt-Co in 1 liter of water is determined as 1 colour unit on the scale. If water has colour, it indicates potential environmental hazards if not handled properly. Colour content measurements for RBBR waste were carried out at 0, 15, 30, 45 and 60 minutes under optimum operating conditions using UV-Vis spectrophotometry at various time intervals.

3. Results

3.1. Reactor Leak Test

In this test, no leaks were found at all, either from the reactor or hose side. Because the flow rate of the circulating liquid feed is affected by the injection of air into the reactor, the product flow rate increases as the gas flow rate increases. The product flow rate is affected by the flow rates of gas and liquid. Because the gas can keep the liquid for a longer period in the reactor, the mass transfer between the feed gas and the plasma required by the reactor will be more efficient.

3.2. Hydroxyl Radical Quantification Test

The number of hydroxyl radicals tends to increase with the length of the process time for all operating conditions, because more ozone is generated. The peak concentration of hydroxyl radicals was at the 30th minute of condition 2, namely 0.22525 mmol.

The 2nd and 4th condition examine the impact of gas type on hydroxyl radical quantification in free air fluid and oxygen. It found that free air fluid generates more hydroxyl radicals than oxygen due to heat accumulation over time. Oxygen fluid, with a high purity of 92% to 96%, produces more reactants for ozone production than air. As the reactor produces more heat, the reaction generation shifts towards reactants. Ozone can be easily decomposed into oxygen under high temperatures. The mechanism also influences test outcomes by generating hydroxyl radicals (Hama Aziz et al., 2018).

$$H_2O + e^- \rightarrow OH^\bullet + H^\bullet + e^- \quad (1)$$
$$2H_2O + e^- \rightarrow H_2O_2 + H_2 + e^- \quad (2)$$
$$2OH^\bullet \rightarrow H_2O_2 \quad (3)$$
$$O^\bullet + H_2O \rightarrow 2OH^\bullet \quad (4)$$
$$H_2O + OH^\bullet \rightarrow HO_2^\bullet + O_2 \quad (5)$$
$$OH^\bullet + H^\bullet \rightarrow O^\bullet + H_2 \quad (6)$$

Furthermore, the formation of hydroxyl radicals is inversely proportional to the rise in plasma voltage. The heat generated by the reactor because of the high plasma voltage impacts the ozone formation process, which tends to move towards the reactants. Finally, the amount of ozone and hydroxyl radicals generated decreases.

3.3. Ozone Solubility Test

In the experiment, it was observed that ozone exhibited the highest solubility in condition 4, while the lowest solubility was observed in condition 2. The reasoning behind this phenomenon can be attributed to the gradual increase in the formation of ozone over time. Notably, the maximum level of ozone solubility was recorded during the 30^{th} minute of condition 2.

The production of ozone concentration yielded 0.18 ppm under air gas type conditions, with a gas flow rate of 2 lpm and a plasma voltage of 12 kV. However, for oxygen gas conditions, the gas flow rate and plasma voltage remained the same, with an increase in the ozone concentration to 0.38 ppm. Injected gas sources utilized in the ROPN disintegrate into radicals, which heavily influences the ozone solubility and radical formation. Injecting free air into the reactor produces a higher amount of hydroxyl radicals and nitrogen radicals due to the assumed 21% oxygen and 79% nitrogen composition (Luvita, 2022). On the other hand, using an oxygen concentrator yields superior outcomes.

Ozone solubility rises with plasma voltage because the electrode receives more electrical energy, resulting in an increase in electric field intensity. This happens when gas molecules ionise, lose, or acquire charge as a result of the interaction between the gas fluid and the electrode surface. The stronger the electric field, the more particles and electrons are created, resulting in greater collisions and faster ionisation (Christianti, 2022). Because of the increasing strength of the electric field, more ozone is formed.

Table 1. Hydroxyl Radical Quantification and Ozone Solubility Test Result.

No.	Condition	H_2O_2 (mmol)		Ozone concentration (ppm)	
		15 min.	30 min.	15 min.	30 min.
1	4 lpm air, 5 kV	0.172	0.069	0.087	0.159

No.	Condition	H_2O_2 (mmol)		Ozone concentration (ppm)	
		15 min.	30 min.	15 min.	30 min.
2	2 lpm air, 12 kV	0.133	0.037	0.180	0.225
3	2 lpm oxygen, 5 kV	0.146	0.340	0.340	0.199
4	2 lpm oxygen, 12 kV	0.133	0.570	0.380	0.172

3.4. RBBR Degradation

Gas Flow Rate Variation

The rate of air flow has a significant impact on the degradation of RBBR waste. The smallest degradation percentage is observed at a rate of 2 litres per minute, while the largest is observed at 4 litres per minute. As the degradation process takes longer, the percentage of degradation increases. These results are due to the production of a greater amount of ozone and hydroxyl radicals, which attack the RBBR more rapidly in waste. Higher gas flow rates produce greater degradation.

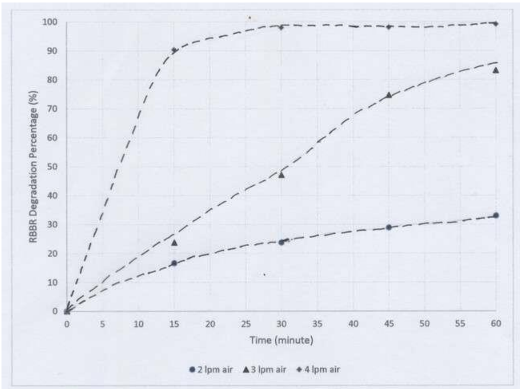

Fig 2. Effect of Gas Flow Rate on RBBR Degradation.

Gas Type Variation

The gas type has a significant impact on the degradation of RBBR waste, with oxygen gas proving to be the most effective. Oxygen enables the RBBR degradation percentage to reach 100%, compared to only 87.54% using free air, which has a lower oxygen content. This leads to a reduced level of effectiveness due to the disturbance of active species, especially hydroxyl radicals. Nitrogen gas, on the other hand, reacts with oxygen to form NO_2, HNO_2, and HNO_3, as it has a higher bond dissociation energy (Zhang et al., 2018). However, oxygen gas with a purity exceeding 90% generates more ozone gas than other gases. This active species reacts rapidly with organic compounds containing double bonds (Von Gunten, 2003), resulting in enhanced efficacy of oxygen gas in breaking down RBBR waste.

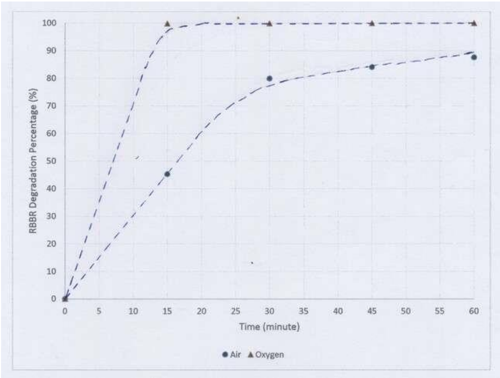

Fig 3. Effect of Gas Type on RBBR Degradation.

Plasma Voltage Variation

Plasma voltage has a significant effect on the degradation of RBBR waste, with 12 kV having the lowest degradation percentage and 5 kV having the highest. Higher plasma voltage results in an increased generation of heat by OPNR, leading to a corresponding rise in ozone-forming reactions. As these reactions progress, reactants begin to shift, and a decline in ozone formation causes a reduction in oxidising compounds. This decrease ultimately results in a less effective degradation of RBBR.

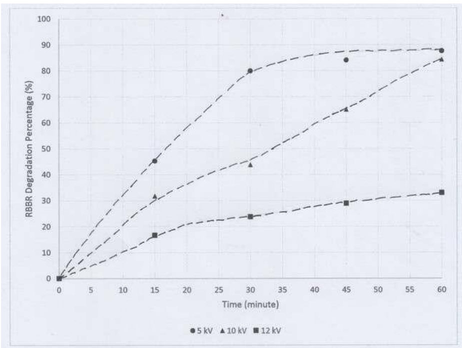

Fig 4 Effect of Plasma Voltage on RBBR Degradation.

3.5. pH Test

Table 3 illustrates a decline in pH over time as degradation continues. This is due to the increased formation of H_2O_2 compounds, which are acidic and result from the recombination of hydroxyl radicals. Furthermore, organic acids, formed as intermediate compounds during RBBR degradation, are increasingly produced with degradation time, thereby lowering the pH of the waste more severely.

3.6. Nitrate Content Test

Nitrate concentration increased with the length of the RBBR waste degrading process, reaching a high at the 60th minute. This is due to the rise of ozone and hydroxyl radicals produced over time, while there are still trace amounts of nitrogen gas in the outflow from the oxygen concentrator. This is what increases the chance of NO oxidation to nitrate.

3.7. COD Content Test

The COD content decreased in the 15th minute and then increased again till the 60th minute. The decrease in COD value until the 15th minute indicates that RBBR is degraded by active species, reducing the amount of oxygen required to oxidise it. Furthermore, even if the percentage of RBBR degradation is 100% at the 60th minute, an increase in the COD value until the 60th minute might suggest that there are chemicals, among others, generated because of RBBR degradation that need to be further oxidised. It is because the oxidized RBBR compound will produce small organic acid molecules after the bonds are broken as a combined intermediate (Gao et al., 2008).

3.8. Pt-Co Scale Test

Pt-Co scale decreased to 0 at 30 minutes and then increased slightly at 45 to 60 minutes. This shows that ROPN has succeeded in degrading RBB-R waste and changing the colour of the waste to clear.

Table 3. pH, Nitrate Content, COD Content and Pt-Co Scale Test Result.

No.	Time (minute)	pH	Nitrate Concentration (ppm)	COD Content (mg/L)	Pt-Co Scale (ppm)
1	0	5.53	0	56.37	237.30
2	15	3.96	18.42	17.94	27.94
3	30	3.71	34.82	33.88	0
4	45	3.79	38.10	36.73	9.95
5	60	3.60	44.37	48.97	12.25

4. Conclusion

According to the study's results, OPNR proves more efficient in degrading RBBR liquid waste under optimal conditions, such as a plasma voltage of 5 kV, a 2 litres/minute oxygen flow rate, and an initial concentration of 100 ppm. Furthermore, under optimal conditions, the percentage of RBBR degradation amounts to 100%, with a COD content of 48.97 mg/L, a nitrate content measuring 44.37 ppm, and a colour content of 12.25 ppm.

Authors' Contributions

I.J. Kim: Conceptualization, Methodology, Investigation, Visualization, Formal analysis, Writing – original draft, Writing – review & editing. V. Luvita: Conceptualization, Methodology, Validation, Writing – review & editing, Supervision. Y. Muharam: Conceptualization, Methodology, Writing – review & editing, Supervision. S. Bismo: Conceptualization, Validation, Writing – review & editing, Supervision.

Conflicts of Interest

The authors declare they have no conflicts of interest.

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